

REMARKSI. Status of the Claims

Claims 13-17 are pending. Applicants cancel claims 13-17 and present new claims 18-22 in this response. Support for the new claims appears in the application in the original claims, which are redrafted to require the labile X ligands of original claim 2 and a Group 6 metal (chromium, molybdenum, tungsten).

II. Response to Office Communication and Request for Extension of Time

New claims 18-22 read on the previously elected and examined species of (3-(2-pyridylethyl)indenyl)chromium dichloride, so the Examiner should agree that the Applicants have now met the requirements of a fully responsive reply to the Office action mailed April 9, 2008.

Applicants hereby respectfully request a three-month extension of time under 37 C.F.R. § 1.136(a) for reply to the Office action. Applicants have authorized the Commissioner to charge Deposit Account No. 08-2336 in the amount of \$ 1,110.00.

III. Response to the Section 112 Rejection

Claims 1-6 stand rejected under 35 U.S.C. § 112, second paragraph, as indefinite. Applicants have overcome the rejection by cancelling claim 1 and providing in new claim 18 antecedent basis for the X ligands. In view of the amendment, the Examiner should reconsider and withdraw the rejection.

IV. Objection to the Specification

The Examiner objected to the specification because of a nomenclature error. Applicants corrected the error in the response mailed 30 June 2008, so the Examiner should withdraw the objection.

V. Response to the Rejection under Section 103(a)

Applicants traverse the rejection of claims 1-6 under 35 U.S.C. § 103(a) as unpatentable over U.S. Pat. Appl. Publ. No. 2001/0041777 (Meyer et al.), and they respectfully ask the Examiner to reconsider and withdraw the rejection in view of the following remarks.

Meyer teaches supported heterometallocene catalysts wherein the support is a particulate polymeric material (Abstract). The transition metal complex and a boron activator compound are deposited on the support (Abstract). The Examiner noted that suitable complexes are broadly described as having formula $(L^*)_n(L)_mM(X)_y$ where L^* is an anionic polymerization-stable heteroatomic ligand, L could be indenyl, M could be Cr, and the L^* and L ligands could be bridged by an ethylene moiety. Meyer describes particularly advantageous L^* groups as "substituted and unsubstituted boraaryl, pyrrolyl, azaborolinyl, quinolinyl, and pyridinyl ligands" (paragraph [0015]). In the only examples, Meyer uses a particular non-bridged cyclopentadienyl boraarylzirconium complex (see paragraphs [0042] through [0047]). Complexes other than Group 4 complexes are not prepared or tested.

Applicants cancelled claims 1-6 in favor of new claims 18-22, so the issue is whether the new claims are patentable over Meyer and other teachings in the art. Applicants' independent claim 18 defines Group 6 metal indenyl complexes that are bridged by a two- or three-atom group (Z) to an unsubstituted, substituted, or fused heteroatomic ring system (A).

Meyer fails to fairly teach or suggest the now-claimed complexes. In particular, Meyer teaches Group 6 complexes only in the most general sense, as a subclass of Group 3-10 metals; the only examples are with a single zirconium (Group 4) complex. Meyer generally describes bridged complexes, but the only example shown in the reference is an unbridged complex. Finally, Meyer discloses pyridyl groups, but not the specifically claimed combination of a pyridyl group bridged through a two- or three-atom bridge to a cyclopentadienyl system in a Group 6 metal complex.

As those skilled in the art well appreciate, the difference between a Group 4 and a Group 6 metal, without more, is substantial. Even among just chromium complexes, dramatic changes can result from relatively minor adjustments in the ligand environment. See, for example, Y. Liang et al., Organometallics 15 (1996) 5284 at 5285, where certain constrained-geometry complexes of chromium (which are closer in structure to Applicants' claimed complexes than those depicted in Meyer) polymerized ethylene alone but failed to give a copolymer when the reaction was performed in the presence of 1-hexene.

Meyer's complexes may be used only with a "particulate polymeric" support and only with a boron activator. In the examples, Meyer uses Microthene FN 510, a low density polyethylene powder having a particle size of about 20 microns, to support the complex. There is no suggestion in Meyer that the complexes could be used either unsupported, or even supported on a more conventional material such as silica. In fact, the converse is true: a skilled person appreciates that selection of the particulate polymeric support is an important aspect of Meyer's invention that cannot be modified. Meyer also uses trietyl tetrakis(pentafluorophenyl)borate ("F20"), an ionic borate activator, which is a costlier alternative to alumoxanes. In contrast, Applicants demonstrated (see Example 9 and Table 2) that complexes of the invention can be used successfully without a support, and using MAO to activate the complex. Nothing in Meyer suggests that either of these modifications could be made to Meyer's catalysts without detrimental consequences.

Given the substantial differences between the claimed complexes and those disclosed in Meyer, Applicants have no burden to show criticality or unexpected results from the claimed complexes. However, Applicants' catalyst systems that incorporate the claimed complexes are highly productive, incorporate comonomers well to give low density (0.89 to 0.93 g/cm³) polymers, and display good activity at relatively low molar ratios of alumoxane to transition metal (see p. 56 and Table 2). None of these attributes of the particularly claimed complexes were apparent from Meyer or other related teachings.

In sum, Applicants' claimed complexes meet the patentability requirements of Section 103.

VI. Conclusion

In view of the remarks above, Applicants respectfully ask the Examiner to enter the amendments, reconsider and withdraw the rejections, and pass the case to issue. Applicants invite the Examiner to telephone their attorney at (610) 359-2276 if she believes that a discussion of the application might be helpful.

I hereby certify that this correspondence is being deposited with the United States Postal Service as first-class mail, with sufficient postage, in an envelope addressed to: Commissioner for Patents, P.O. Box. 1450, Alexandria, VA 22313-1450 on October 6, 2008.

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Constrained Geometry Chromium Catalysts for Olefin Polymerization

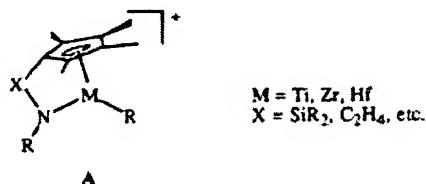
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Summary: Chromium(III) alkyls featuring an amido ligand tethered to a permethylcyclopentadienyl ring (i.e. $[\eta^5\text{-Me}_4\text{CsSiMe}_2\text{-}\eta^1\text{-}N\text{Bu}]\text{CrR}_2$) have been prepared and structurally characterized. They catalyze the polymerization of ethylene and the dimerization and isomerization of α -olefins.

Among the metallocene catalysts currently revolutionizing the field of Ziegler-Natta catalysis,¹ so-called constrained geometry molecules (see A)—i.e. metal



complexes containing an amide ligand tethered to a cyclopentadienyl group—play a special role as copolymerization catalysts.² The sterically unencumbered nature of the catalytic site is thought to facilitate incorporation of various α -olefins into growing polymer chains. Extension of this structural feature to chromium, one of the metals employed commercially in coordination polymerization,³ might thus be expected to generate a new family of Cr-based copolymerization catalysts. Herein we report the synthesis and characterization of the first constrained geometry chromium alkyls and an investigation of their reactivity with olefins.

Slow addition of $\text{Li}_2(\text{THF})_n[\text{Me}_4\text{C}_5\text{SiMe}_2\text{N}^*\text{Bu}]^4$ to a suspension of $\text{CrCl}_3(\text{THF})_3$ in THF at low temperature afforded dark green ($\text{Cp}^*\text{SiNR})\text{CrCl}(\text{THF})$ (1) in 68% yield. Alkylation of this starting material with various lithium alkyls yielded a new class of chromium(III) alkyls (see Scheme 1). Depending on the steric bulk of the alkyl group, the complexes either retained or lost the THF ligand; in the latter case (e.g. when $\text{R} = \text{CH}_2\text{SiMe}_3$) a coordinatively unsaturated metal alkyl akin

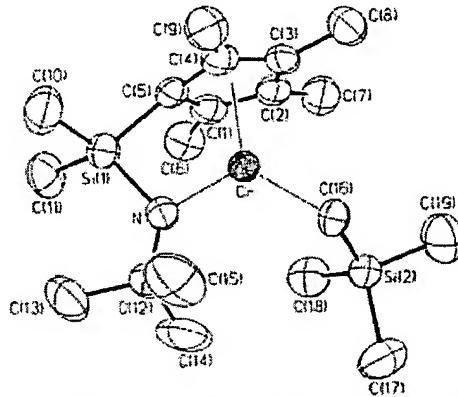


Figure 1. Molecular structure of (Cp^*SiNR) $\text{CrCH}_2\text{SiMe}_3$ (4). Selected interatomic distances and angles: Cr–N, 1.920(4) Å; Cr–C(16), 2.092(5) Å; Cr–C_{cp,av}, 2.23 Å; N–Cr–C(16), 113.8(2)°; Cp_{centroid}–Cr–N, 115.9°; Cr–C(16)–Si(2), 119.6(3)°.

To A was isolated. Figure 1 shows the result of a crystal structure determination of $(\text{Cp}^*\text{SiNR})\text{CrCH}_2\text{SiMe}_3$ (4),⁵ a brown solid that is freely soluble in hydrocarbon solvent. The molecule has approximate mirror symmetry; the idealized mirror plane bisects the chelating ligand, and the alkyl carbon directly bonded to chromium deviates only very little from it (0.26 Å). The three-coordinate nitrogen is planar (sum of angles: 359.2°), and the Cr—N (1.92 Å) distance is considerably shorter than the Cr—C(16) bond (2.09 Å), the latter an entirely normal chromium(III)—carbon single-bond distance.⁶ Both observations are consistent with some degree of ligand-to-metal π -donation involving the amide ligand, albeit not sufficient for a full Cr=N double bond (ca 1.65 Å).⁷ The effective magnetic moment of the complex measured $\mu_{\text{eff}}(\text{RT}) = 4.0(1) \mu_{\text{B}}$, consistent with three unpaired electrons. Thus the π -acceptor orbital on the metal must be singly occupied, and the N-Cr π -bond is a three-electron interaction of attenuated strength. The $\text{Cp}^*_{\text{centroid}}\text{—Cr—N}$ angle of 115.9° is an indication of the “openness” of the structure adjacent to the Cr—C bond, i.e. the anticipated site of catalytic activity. Despite its coordinative and electronic unsaturation, 4 exhibited no indication of an agostic interaction,⁸ e.g. with one of the methyl hydrogen atoms of the

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(4) (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* 1990, 9, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* 1994, 116, 4623.

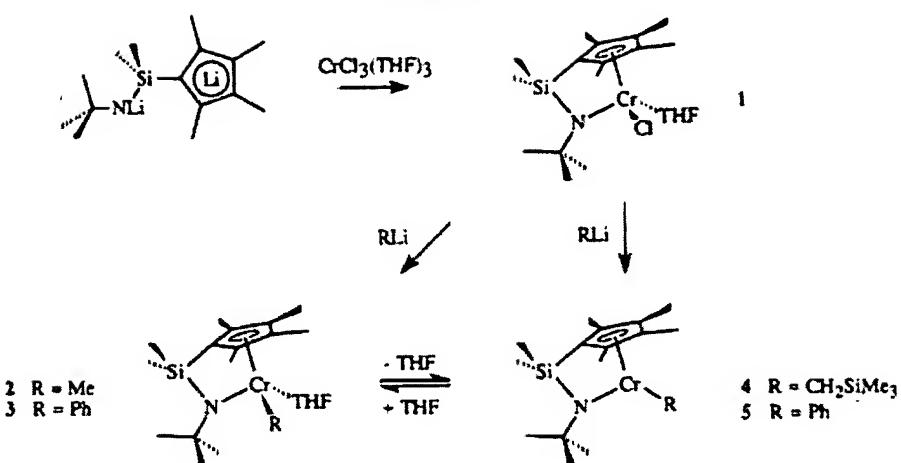
(5) 4: $C_{19}H_{38}CrNSi_2$, triclinic $P\bar{1}$, $a = 9.186(1)$ Å, $b = 9.678(1)$ Å, $c = 13.745(1)$ Å, $\alpha = 94.803(9)^\circ$, $\beta = 100.434(8)^\circ$, $\gamma = 102.05(1)^\circ$, $Z = 2$, $T = 297$ K, $R = 5.30\%$, $R_w = 6.24\%$.

(6) Theopold, K. H. *Acc. Chem. Res.* 1990, 23, 263.

(7) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; p 180.

(8) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* 1988, 36, 1.

Scheme 1



nethylsilyl)methyl ligand. Such interactions—at least in the ground state—would not appear to be important in chromium catalysis.⁹

We have previously established the minimum requirements for ethylene polymerization activity of organochromium catalysts, namely a chromium(III)—carbon σ -bond and coordinative unsaturation (i.e. pseudo-five-coordination in a cyclopentadienyl complex).¹⁰ Complex 4 fits this description, and accordingly it catalyzed the polymerization of ethylene. Exposure of a toluene solution (50 mL, 3.0 mM) at room temperature to ethylene (500 psi) for 3.5 h yielded 2.6 g of polyethylene. When the same polymerization reaction was carried out in a 1:1 mixture of toluene and 1-hexene, 2.1 g of polymer was formed.¹¹ By ^{13}C NMR, this material showed no evidence for incorporation of the α -olefin! Despite the great concentration advantage of the hexene the catalyst selectively polymerized only ethylene. Attempts to polymerize propene, using 4 as a catalyst, were unsuccessful. However, when the reaction of 4 with propene

at room temperature was monitored by ^1H NMR, complete conversion to 2-methyl-1-pentene was observed over the course of several hours (the product was identified by ^1H and ^{13}C NMR). While “constrained geometry” chromium catalysts can apparently bind and insert α -olefins, the latter do not compete effectively with ethylene for incorporation into a growing polymer chain, and chain transfer by β -hydrogen elimination must be very facile for chromium alkyls featuring tertiary C—H bonds at the β -carbon atom.

Several observations are relevant to a consideration of the mechanism for the olefin dimerization reaction noted above. The isotropically shifted resonances of 4

remained constant during this transformation, and no new paramagnetic compounds were observed by ^1H NMR; furthermore, no organic compounds containing (trimethylsilyl)methyl groups were observed by NMR. Reaction of 1-hexene with 4 yielded not only the expected product of head-to-tail dimerization, i.e. 2-butyl-1-octene, but also a mixture of isomeric internal hexenes. Thus 4 catalyzes the isomerization of olefins as well. Finally, both the dimerization and isomerization were accelerated by the addition of hydrogen (e.g. 300 Torr H_2). On the basis of these observations, we suggest that the actual catalyst may be the hydride $[(\text{Cp}^*\text{SiNR})\text{CrH}]_n$, small quantities of which may be formed by β -elimination from $(\text{Cp}^*\text{SiNR})\text{CrCH}_2\text{CH}_2\text{SiMe}_3$, i.e. the product of insertion of an olefin in the chromium—carbon bond of 4. Indeed, prolonged exposure of 4 to H_2 yielded SiMe_4 and at least one new, and as yet unidentified, paramagnetic compound. Efforts to characterize this species fully are under way.

The catalytic regiospecific head-to-tail dimerization of olefins may have applications in organic synthesis,¹² and we have tested a number of substrates to begin to delineate the scope of this transformation. Styrene or 3,3-dimethyl-1-butene did not react under these conditions. 1,5-Hexadiene yielded solely methylenecyclopentane, and 1,6-heptadiene gave methylenecyclohexane and 1-methyl-2-methylenecyclopentane in a 3:1 ratio. We are currently exploring the utility of 4 and its analogues for cyclizations of more complex organic substrates.

Our understanding of organochromium chemistry related to olefin polymerization has reached the stage where molecular design of catalysts is feasible. However, simple extrapolation of design principles from group 4 chemistry to the later metal fails, and a homogeneous chromium-based copolymerization catalyst remains elusive. The available evidence suggests that cyclopentadienylchromium(III) complexes feature

(9) For the role of such interactions in metallocene catalysis with earlier metals, see: Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* 1996, 29, 85.

(10) (a) Thomas, B. J.; Noh, S.-K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* 1991, 113, 893. (b) Bhandari, G.; Kim, Y.; McFurlan, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* 1995, 14, 738.

(11) (a) Toluene: $M_w = 65720$, $M_w/M_n = 52$. (b) Toluene/1-hexene: $M_w = 102\,300$, $M_w/M_n = 37$. Note that these numbers reflect bimodal product distributions with most of the samples being of low molecular weight ($M_w = 1000$ –10 000). A possible explanation for this observation (suggested by a reviewer) is the presence of small amounts of a chromium alkyl resulting from cleavage of the Cp^* —Si bond during the synthesis (i.e. a compound containing a $\text{C}_5\text{H}_5\text{Me}_4$ ligand); such fragmentation has been noted in group 4 chemistry, and low levels of contaminants would be hard to detect in paramagnetic Cr complexes.

(12) (a) Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* 1996, 118, 4715. (b) Shaughnessy, K. H.; Waymouth, R. M. *J. Am. Chem. Soc.* 1995, 117, 5873. (c) Negishi, E.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* 1994, 116, 8404. (d) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* 1992, 114, 3123. (e) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* 1990, 74. (f) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, 102, 5610.

highly disparate rates of chain growth for ethylene and α -olefins.¹³ Our results militate against a steric origin of this selectivity; the relevant electronic factors may influence both olefin binding and/or the migratory insertion step. That chromium is capable of copolymerization is demonstrated by the Phillips catalyst (inorganic Cr/SiO₂).³ Homogeneous complexes more closely related to its active site are reasonable synthetic targets in our quest for novel chromium catalysts.

(13) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics*, in press.

Acknowledgment. This research was supported by research grants from the NSF (CHE-9421802) and Chevron Chemical Co.

Supporting Information Available: Tables giving a summary of the crystal structure determination, positional and thermal parameters, and bond distances and angles of 4 and text providing syntheses and spectroscopic data for all complexes (10 pages). Ordering information is given on any current masthead page.

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